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## Coating of Ultrathin Polymer Films on Carbon Nanotubes by a Plasma Treatment

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### ABSTRACT

Ultrathin polymer films have been deposited on both single- and multi-wall carbon nanotubes using a plasma polymerization treatment. HRTEM experiments showed that an extremely thin film of the pyrrole layer (2-7 nm) was uniformly deposited on the surfaces of the nanotubes including inner wall surfaces of the multi-wall nanotubes. Time-of-Flight Secondary ion mass spectroscopy (TOFSIMS) experiments confirmed the nanosurface deposition of polymer thin films on the nanotubes. The deposition mechanisms and the effects of plasma treatment parameters are discussed.

### INTRODUCTION

Nanotubes are used in many applications because of their desirable bulk properties. Unfortunately, the surface of the nanotubes is often not ideal for the particular application. The ability to deposit well-controlled coatings on nanotubes would offer a wide range of technological opportunities based on changes to both the physical and chemical properties of the nanotubes. Atomic layer controlled coatings on nanotubes, for example, would allow nanotubes to retain their bulk properties but yield more desirable surface properties. These ultrathin coatings could act to activate, passivate or functionalize the particle to achieve both desirable bulk and surface properties. For instance, nanophase polymers typically consist of a hard phase dispersed in a soft phase to achieve specific enhanced properties. "Hard" nanotube serves as the hard phase. By manipulation of the physical, chemical and optical properties of the "hard" phase nanotubes, tunable materials properties can be achieved. A key aspect of being able to manipulate the properties of the nanotubes is the surface treatment of the nanotubes by various processing techniques. This technology produces high-tech properties with the low cost normally associated with plastics.

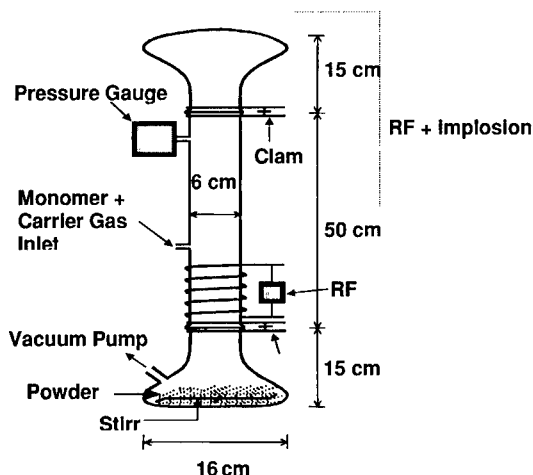
Another example is the consolidation at low temperatures via so-called nanoglu. When an adhesive thin film is coated on the nanotube surfaces, these nanotubes can be consolidated at a temperatures. However, this method requires the adhesive thin film to be extremely thin and uniform. Therefore the volume percent of the polymer is limited to only a few percent. In this way, the bulk mechanical properties can be maintained.

Depositions of ultrathin films with unique physical, chemical and biological properties on nanotubes can also have great potential in many engineering applications.

On the surface of the nanotubes, an extremely thin layer of polyacrylic film can be coated by a plasma treatment. The polyacrylic film will react with metallic ions in water. As a result of the high surface-to-volume ratio of these nanostructured clusters, the efficiency of ion exchange in the water flux is much higher than other types of traditional reactors. Therefore, tailoring the nanotube surface structure becomes of ultra importance in today's nanotechnology. The broad range of these properties due to nano surface structures include electro-magnetic conductivities, uniformity, index of refraction, high reflectance, low absorption, stress, and the adhesion of the film structure to the substrate. All these properties are determined by new parameters such as interfaces between the ultrathin film and the nanotube, nanotube surface morphology, and structures of the film.

## EXPERIMENTAL DETAILS

In this experiment, we used Pyrograf III PR-24-PS and PR-24-HT (17) nanotubes as substrates. These are the multi-wall carbone nanotubes (MWCNT). Single-wall carbon nanotubes (SWCNT) were also used for plasma treatment. These nanotubes have the same structure and purchased from Pyrograf products Inc. The schematic diagram of the plasma reactor for thin film deposition of nanotubes is shown in Fig. 1. The vacuum chamber of the plasma reactor consists of a Pyrex glass column about 80 cm in height and 6 cm in internal diameter. The carbon nanotubes are vigorously stirred at the bottom of the tube and thus the surfaces of nanotubes can be continuously rotated and exposed to the plasma for thin film deposition during the plasma polymerization process. A magnetic bar was used to stir the powders. The gases and monomers were introduced from the gas inlet during the plasma cleaning treatment or plasma polymerization. The system pressure was measured by a thermocouple pressure gauge. A RF power generator operating at 13.56 MHz was used for the plasma film deposition (7,8).



**Figure 1.** Schematic diagram of the plasma reactor for thin polymer film coating of the nano-particles.

Before the plasma treatment, the chamber pressure was pumped down to less than 5 Pa at which time the monomer vapors were introduced into the reactor chamber. The operating pressure was adjusted by the mass flow controller. Pyrrole was used as the monomer for plasma polymerization. To be able to distinguish the deposited polymer thin film and the surface of carbon nanotubes, we introduced a small fraction of  $C_6F_{14}$  to copolymerize with the pyrrole monomer. In this way, we will be able to characterize the deposited thin film in the TOFSIMS experiments. During the plasma polymerization process, the RF power was 15 W and the system pressure was 30 Pa. The plasma treatment time was 30 minutes per batch of 0.3 grams of powder.

After the plasma treatment, the carbon nanotubes were examined using transmission electron microscopy (TEM) and Time-of-Flight secondary ion mass spectroscopy (TOFSIMS). The high-resolution TEM experiments were performed using a JEOL JEM 2010F electron microscope with a field emission source. The accelerating voltage was 200 kV. The nanotubes were dispersed in methanol and suspended on a perforated carbon film supported by Cu grids. Bright-field and high-resolution imaging techniques were used to characterize the features of both the original and the coated carbon nanotubes. TOFSIMS was performed on a Ion-Tof model IV equipped with a 25 keV 69Ga<sup>+</sup> source. The mass resolution of the instrument was 8,000 at amu 28. Positive and negative spectra were collected in the mass range 0-1000 amu. The spectra were acquired by rastering the beam over an areas of 300 x 300  $\mu m$  of bundle of the untreated or treated carbon nanotubes.

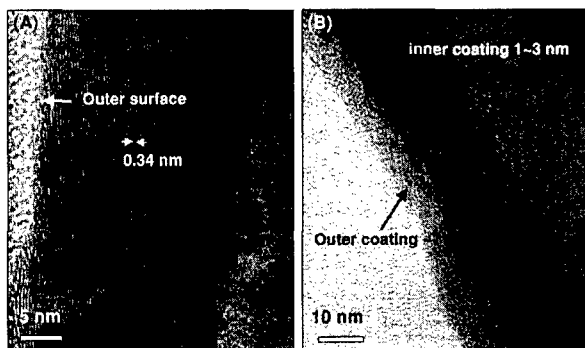
Fig. 2 shows the bright-field TEM images of the original uncoated Pyrograf III PR-24-HT (Fig. 2A) nanotubes and the Pyrograf III PR-24-PS carbon nanotubes (Fig. 2B). As can be seen in this figure, both Pyrograf III carbon nanotubes have similar size features with a hollow channel. The Pyrograf III PR-24-HT nanotubes have slightly smaller outside diameters averaging about 70 nm, and they are quite uniformly distributed. The Pyrograf III PR-24-PS carbon nanotubes have outside diameters ranging between 40 nm and 120 nm. Some nanotubes become curved during their growth with the open ends. An HRTEM image (Fig. 3A) of the original Pyrograf III PR-24-HT carbon nanotubes shows the graphite structure with the interlayer spacing  $d_{002}=0.34$  nm. Based on the bright-field TEM and HREM images, the wall thickness of the nanotubes can be estimated to be about 20~30 nm for both the Pyrograf III PR-24-HT and Pyrograf III PR-24-PS carbon nanotubes. Nanotubes with axially parallel graphite layers (not shown here) and nanotubes with axially parallel graphite layers oriented at an angle to the tube axis (Fig. 3A) were observed. The edge dislocations can be seen due to the disorder of the graphite layers (002). It is noticed that both the outer and inner surfaces terminate at the graphite (002) layer without the addition of a surface layer, for the originally uncoated nanotubes (Fig. 3A). The bright field and high-resolution TEM images of these nanotubes after plasma treatment are shown in Fig. 3B (Pyrograf III PR-24-PS PR-24-HT nanotubes). An ultrathin film amorphous layer can be clearly seen covering both the inner and outer surfaces of the Pyrograf III PR-24-HT nanotubes (Fig 3B). The thin film is uniform on both surfaces, however, with a larger thickness on the outer wall (7 nm) than on the inner wall (1~3 nm) surface (Fig. 3B). The thickness of ultrathin film is approximately 2~7 nm all the way surrounding the nanotube surfaces for both the Pyrograf III PR-24-HT and Pyrograf III PR-24-PS carbon nanotubes. The film is also thicker and more uniform than the roughness (<1 nm) on the outer surface of the carbon

nanotubes (Fig. 3A). The lattice image of graphite can be clearly seen with an extremely thin layer of polymer film on its surface.

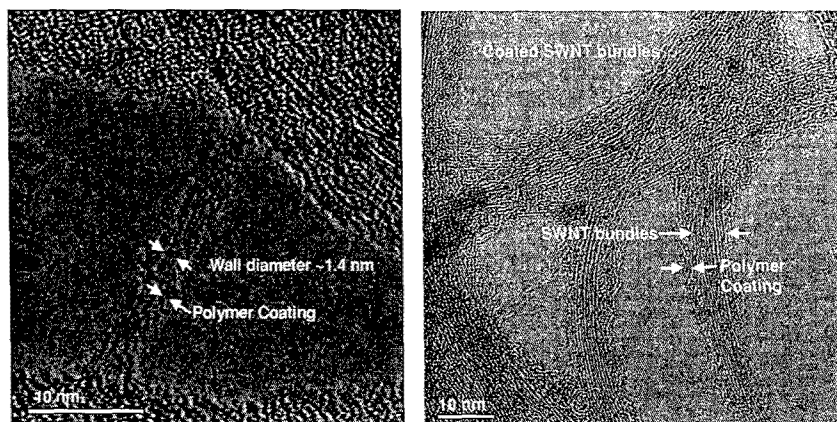
Figure 4a is the HREM image of the coated SWCNT. Compare to Figure 2 and 3, one can see a much thinner nanotube with a diameter of only 1.4 nm. Figure 4b is the HRTEM image of coated SWCNT in a bundle. Due to high surface energies, these SWCNT's tend to cluster together in an aligned form. The polymer film, however, is deposited on the outer surface of the bundle as show in Figure 4b.



**Figure 2** Bright-field TEM images of the original uncoated carbon nanotubes of Pyrograf III PR-24-PS PR-24-HT (A) and Pyrograf III PR-24-PS (B).



**Figure 3.** HRTEM images of yrograf III PR-24-PS PR-24-HT nanotube: (A) The fragments of the wall with inclined planes (002) showing lattice space on the outer and inner surfaces of uncoated Pyrograf III PR-24-PS PR-24-HT nanotubes with slight roughness ( $<1$  nm) on the surface; (B) An ultrathin film of pyrrole can be observed on both outer and inner surfaces of coated Pyrograf III PR-24-PS PR-24-HT nanotubes.



**Figure 4.** HRTEM images of single wall carbon nanotubes: (A) an isolated SWCNT coated with pyrrole; (B) a bundle of SWCNT coated with pyrrole.

To confirm the TEM observations shown in Fig. 2-4, TOFSIMS was carried out to study the surface films of the nanotubes. Fig. 5a shows part of the TOFSIMS spectra of untreated Pyrograf III PR-24-HT carbon nanotubes. The spectrum of the untreated nanotubes show an appreciable intensity of carbon, hydrogen, and oxygen, which is a characteristic of a un-treated natural surface. In Fig. 5b one can see that the treated nanotubes have strong carbon-fluorine peaks indicating the surface coating of the nanotubes and consistent with the HRTEM data presented in Fig. 2-4. In particular, the spectrum in Fig. 5b shows carbon-fluorine in the forms of  $C_4F_7^+$ ,  $C_3F_7^+$ ,  $C_4F_6^+$ ,  $C_5F_7^+$  indicating highly branched and cross linked polymer structure in the deposited thin film. It is to be noted that the fluorine shown in the TOFSIMS spectrum can only be part of the monomer introduced during the plasma coating process, a strong indication of polymerized film on the carbon nanotubes.

During coating, the polymer is introduced as a vapor and the collision frequency increases with the gas pressure. The rate of polymer condensation on the nanoparticle surfaces may be influenced by many parameters such as electron density, temperature, and energy density. To achieve a thin and uniform coating on such small nanoparticles, all these synthesis parameters must be optimized. Although a systematic study on the optimization of synthesis parameters has not yet been carried out, the preliminary experimental data have indicated that the coating polymer must be stable and not reactive with the substrate during coating. The gas pressure must be moderate for a low collision rate on the nanoparticle surfaces. In addition, polymerization should take place relatively fast after the condensation on the particle surfaces. These will ensure a uniform coating on the order of 1-2 nm for all particle sizes.

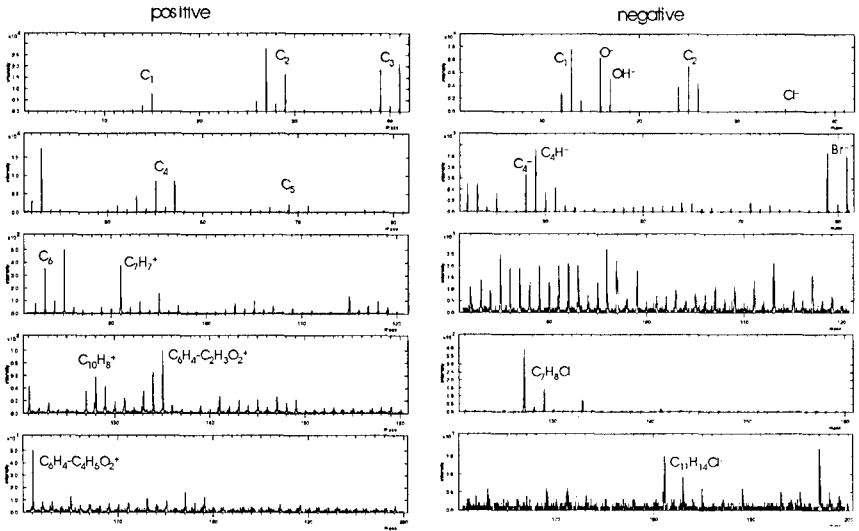


Figure 4. SIMS data showing uncoated MWCNT's..

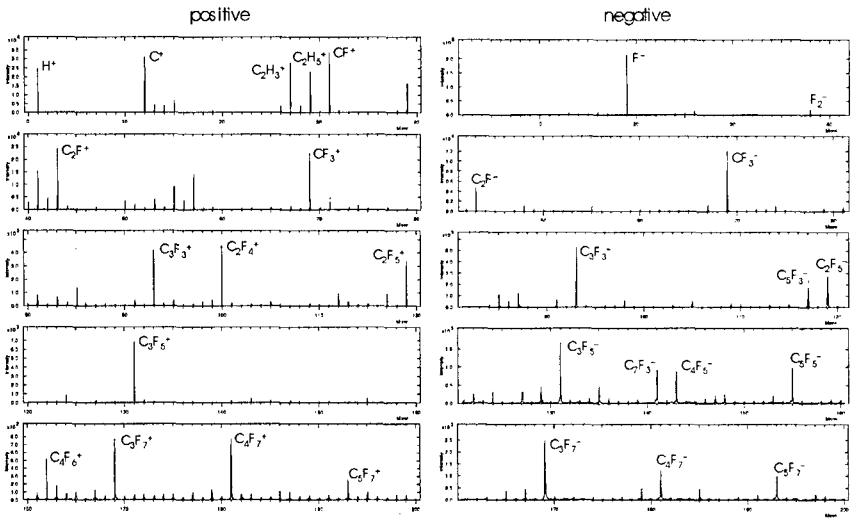


Figure 5. SIMS data showing coated MWCNT's.

In summary, we have deposited an ultrathin polymer film on the inner and outer surfaces of carbon nanotubes by means of a plasma polymerization treatment. The polymer layer is not only uniform on both inner and outer surfaces, but it is also deposited in an extremely thin layer of 2~7 nm. TOFSISM spectra confirmed the polymer nature of the deposited thin films. By controlling the plasma coating conditions, the deposition rate can be closely controlled so that the film thickness on both the inner and outer wall surfaces is uniform and nearly identical.

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